

Off-the-Shelf Antifreeze Admixture For Concrete

Initial Laboratory Investigation

Charles J. Korhonen and Sherri A. Orchino

January 2001

Abstract: Set-controlling and water-reducing admixtures conforming to ASTM C 494 were studied for their effect on strength gain of portland cement concrete at below-freezing temperatures. Because standard practice does not limit the number of admixtures that can be used in concrete, the objective was to use as many admixtures as necessary to depress the freezing point of the mix water to -5°C (23°F) or

below and to promote strength gain reasonably quickly. A combination of set accelerators with water reducers showed promise of promoting significant strength gain at nearly -10°C (14°F), but at the sacrifice of workability. More work needs to be done to develop a combination of off-the-shelf admixtures that will permit concreting at temperatures as low as -10°C (14°F).

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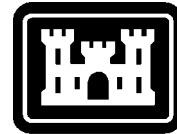
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Technical Report
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Prepared for
OFFICE OF THE CHIEF OF ENGINEERS

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PREFACE

This report was prepared by Charles J. Korhonen, Research Civil Engineer, Civil Engineering Research Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Engineer Research and Development Center (ERDC), Hanover, New Hampshire, and by Sherri A. Orchino, Civil Engineering Technician, Civil Engineering Research Division, CRREL. Asok Sarkar, formerly of the University of Dayton Research Institute, provided the input for Appendix A.

The authors thank Guy Berthiaume and Craig Graham from the Transportation Departments of Maine and Vermont, respectively, and members of their staffs for technically reviewing this report.

Funding for this work was provided by DA Project 4A762784AT42, Cold Regions Engineering Technology, Work Package 162, Cold Regions Theater of Operations Engineering, and Work Unit TOØ11, Expedient Cold Weather Admixtures.

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INTRODUCTION

It has long been a goal of the concrete industry to emplace fresh concrete during the winter without thermal protection. A few years ago private industry essentially achieved that goal by developing two prototype antifreeze admixtures (Korhonen and Brook 1996, Korhonen et al. 1997b). The prototypes enabled concrete to gain strength and to resist freezing down to -5°C (23°F); normal concrete freezes at these temperatures. However, partly because of resistance to change and partly to find an admixture that works at lower temperatures, antifreeze admixtures have not been made available to the general public.

In 1998, we reported that we did not have to wait until the ultimate antifreeze admixture was marketed—an interim one could be formulated from the admixtures already developed for concrete. In a study conducted for the Tennessee Valley Authority (TVA), an antifreeze admixture was successfully fashioned from the seven categories of set-controlling and water-reducing admixtures approved for use in concrete by ASTM C 494 (ASTM 1997c, Korhonen et al. 1998). Combining set-accelerators with other chemicals that could act as freezing point depressants developed the admixture. Not only did the admixture protect the concrete from freezing, it also was immediately acceptable to TVA engineers because its components complied with ASTM C 494.

It was apparent from the TVA study that more could be done to optimize these chemicals for use at low temperature and to develop protocol for their use. This paper reports on the initial laboratory study to develop an antifreeze admixture from commercial admixtures. Work is continuing.

TEST PROGRAM

The objective of this study was to explore the low-temperature performance of commercial admixtures that conform to ASTM C 494. A number of companies sell these admixtures, but because of study constraints, admixtures from only one company were chosen. (A follow-on study should be conducted to evaluate admixtures from the other companies, as some admixtures might perform better than those of this study. The follow-on study should also consider compatibility between the chemicals of one company versus another, as it might be best to combine admixtures from different companies.) The prototype admixtures mentioned above would serve as the benchmark against which the formulations tested in this study could be judged.

Admixtures

Neither the manufacturer nor its product names will be disclosed in this report. The admixtures chosen met one or more of the requirements of six of the seven ASTM categories. Table 1 lists those categories, their functions, and their affect on initial setting. The category omitted was Type G, high-range water reducing and retarding admixtures. It was felt that the water reducing and retarding function available in Type D made Type G unnecessary for this test. In addition, calcium chloride, being perhaps the oldest and best-known accelerating admixture, was added to this group.

The ASTM categories serve a variety of functions. Water-reducing admixtures lessen the amount of water required to maintain workability and consequently the amount of water that has to be protected from freezing. Accelerating admixtures speed up the normal process

Table 1. ASTM C 494 admixtures.

<i>Category</i>	<i>Function</i>	<i>Initial set time, deviation from control</i>
A	Water-reducing	1 hr earlier to 1.5 hr later
B	Retarding	1–3.5 hr later
C	Accelerating	1–3.5 hr earlier
D	Water-reducing and retarding	1–3.5 hr later
E	Water-reducing and accelerating	1–3.5 hr earlier
F	High-range water-reducing	1 hr earlier to 1.5 hr later
G	High-range water-reducing and retarding	1–3.5 hr later

None of the manufacturer's admixtures conforming to this standard contained added chlorides. Setting times are based on tests conducted at 23°C.

of hydration. Their advantage in the cold is that the earlier the cement consumes water, the earlier the concrete becomes immune to frost damage. Retarders slow down cement hydration, making them useful for off-setting early stiffening caused by high temperatures or high accelerator doses.

Mortar vs. concrete

Instead of concrete, mortar was used to evaluate the performance of each admixture. Mortar simplified mixing operations, reduced material handling procedures, and permitted smaller test specimens. To the admixture, mortar acts like concrete. It has the same cement and water to react with, similar void spaces to fill, and the familiar aggregate-to-paste transition zones to deal with. The only difference between mortar and concrete is that mortar does not contain coarse aggregate where concrete does.

The mortar consisted of one part Type I portland cement (Table 2) to 2.8 parts ASTM C 33 (ASTM 1997a) sand on a weight basis. The cement-to-sand ratio used in this study is not a ratio typical to concrete but it is a ratio commonly used in mortar studies (ASTM

C 109 [ASTM 1989a]). The mortar intentionally was made without an air-entraining admixture to avoid strength variations caused by variable air contents.

The mortar was mixed in a Hobart mixer according to ASTM C 305 (ASTM 1989b). All but the high-range water reducers were incorporated into the mixing water before being placed in the mixing bowl (high-range water reducers were added during the final minute of mixing). The mixer was run at low speed while the cement was added to the water for 30 seconds. Mixing was stopped, the sides of the bowl were scraped down, and mixing ran for another 45 seconds while sand was added. The mixer was then stopped for a minute and a half before running at medium speed for the final minute.

Test procedure

Five commercial admixtures plus calcium chloride were tested for their effects on fresh and hardened properties of mortar. All tests were compared to control mortar containing no admixtures and all mixing took place at room temperature.

On the fresh mortar, each admixture was evaluated for its effect on flow (workability), setting time (early-age hydration rate), and freezing point depression (frost resistance). The commercial admixtures were tested at their lowest and highest doses recommended by the manufacturer, while the calcium chloride was tested at its maximum allowable dose (2% by weight of cement). Flow tests were conducted according to ASTM C 109 (ASTM 1989a), setting times according to ASTM C 403 (ASTM 1981), and freezing points were obtained from a thermocouple embedded into a dummy cylinder of fresh mortar placed in a coldroom.

Once each admixture was characterized for its effect on fresh mortar, it was combined in various ways to improve the ability of mortar to gain strength at tem-

Table 2. Chemical composition of Dragon Products Co. Type I cement.

<i>Compound</i>	<i>Weight percent</i>
Silicon dioxide	20.6
Aluminum dioxide	4.9
Ferric oxide	2.4
Calcium oxide	63
Magnesium oxide	2.8
Sulphur trioxide	3.3
LOI	1.71
Equivalent sodium oxide	1.32

peratures below freezing. The mortar, mixed at room temperature, was cast into 50.8- \leftrightarrow 101.6-mm plastic cylindrical molds and placed into 20, -5, -10, and -20°C (68, 23, 14, and -2°F) rooms within 30 minutes of the mix water being added to the cement. Three samples from each mix from each temperature were tested in uniaxial compression according to ASTM C 39 (ASTM 1997b) at 7 and 14 days. Prior to testing, the cylinders were stripped from their molds, warmed to 5°C (41°F), and capped with unbonded neoprene held within a steel-retaining cup conforming to ASTM C 1231 (ASTM 1997d). At 14 days, the remaining three cylinders from each mix in each coldroom were moved to the 20°C (68°F) room for an additional 18 days before testing.

RESULTS AND DISCUSSION

Individual admixtures

Table 3 shows the effect of each admixture on the properties of fresh mortar. The admixtures' effect on stiffening is given in terms of setting time. Initial set defines the onset of rigidity—when bleed water disappears and finishing can begin—whereas final set approximates the time when finishing becomes impossible (when measurable strength development begins). For example, a concrete mix containing a mortar fraction similar to that of the control mortar would be expected to be workable for up to 3.2 hours at 19°C

(66.2°F), and following that would have 1.2 hours to be completely finished. Cold weather would increase these times: each 10°C drop in temperature would double them. Thus, anything that can accelerate setting often translates into big savings in time, labor, and money at the construction site, particularly during the winter.

None of the commercial admixtures appeared to accelerate setting. This was not unexpected for the Type A, D, and F admixtures, as they can retard setting (Table 1). However, the Type C and E admixtures, being accelerators, should have reduced the initial and final set times by about one hour (Table 1), but they did not. Instead, both of these admixtures appeared to increase the initial set by more than one hour. Final set was similarly affected. As a possible explanation for the slow setting times, past studies have found that accelerators, when used at higher doses, can prolong setting times (Korhonen et al. 1997a). Another possible explanation for these poor showings could be that the room in which the setting times were done was cooler on the days that the accelerators were tested. Measurements taken later showed that the room did vary by as much as 5°C daily. Since the testing was done over a several-week period, between-test temperature differences are likely. Thus, if, as mentioned earlier, each 10°C drop doubles setting time, a 5°C drop could have easily increased initial set by an hour or more. Time did not allow these setting tests to be repeated. However, the calcium chloride was tested when the room was steady at 19°C (66°F). This time, the initial set was shortened by half

Table 3. Properties of fresh mortar. Set times and flow were conducted at 19°C while freezing points were obtained at -20°C. The letters in column 1 correspond to mortars made with the admixtures of Table 1. Water contents were adjusted so that all mortars had approximately the same flow.

<i>Mortar designation</i>	<i>Initial set (hr)</i>	<i>Final set (hr)</i>	<i>Freezing point (°C)</i>	<i>Flow (%)</i>	<i>w/c ratio</i>
Control	3.2	4.4	-1.9	104	0.48
A – Low dose*	4.7	6	-2.1	102	0.48
A – High dose*	8.5	9.6	-2.3	105	0.45
C – Low dose	4.2	5.75	-1.9	105	0.48
C – High dose	4.0	5.3	-2.7	105	0.47
D – Low dose	5.25	6.5	-1.9	102	0.46
D – High dose	9.4	10.75	-1.9	105	0.46
E – Low dose	4.25	5.4	-2.0	102	0.48
E – High dose	5.0	6.5	-2.7	104	0.42
F – Low dose	4.3	6.0	-1.9	104	0.45
F – High dose	6.1	7.75	-1.9	102	0.39
2% CaCl ₂ †	2.7	4.5	na**	na**	0.48

*Low and high refer to manufacturer's recommendations.

†Maximum dose per cement weight allowed by the American Concrete Institute.

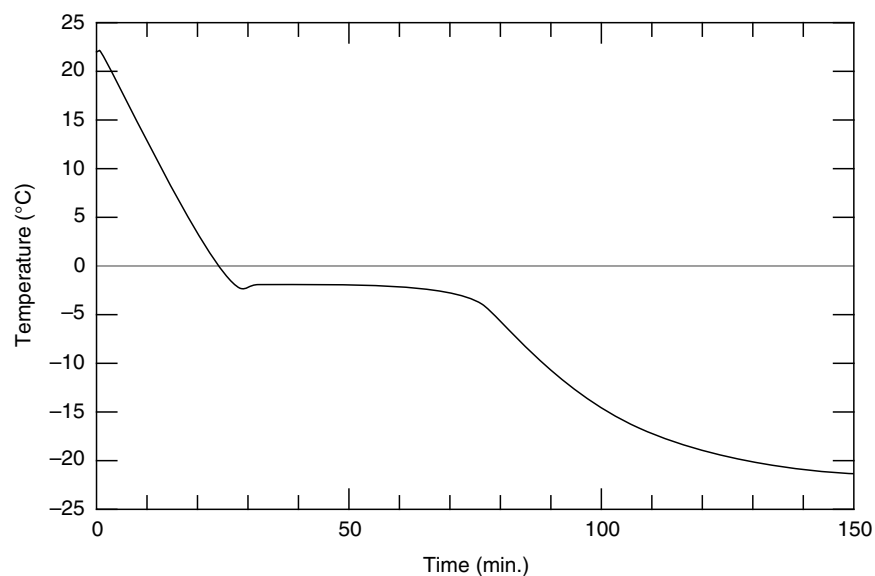
**na means that these tests were not conducted.

an hour compared to control. Better temperature control should produce results that are more consistent.

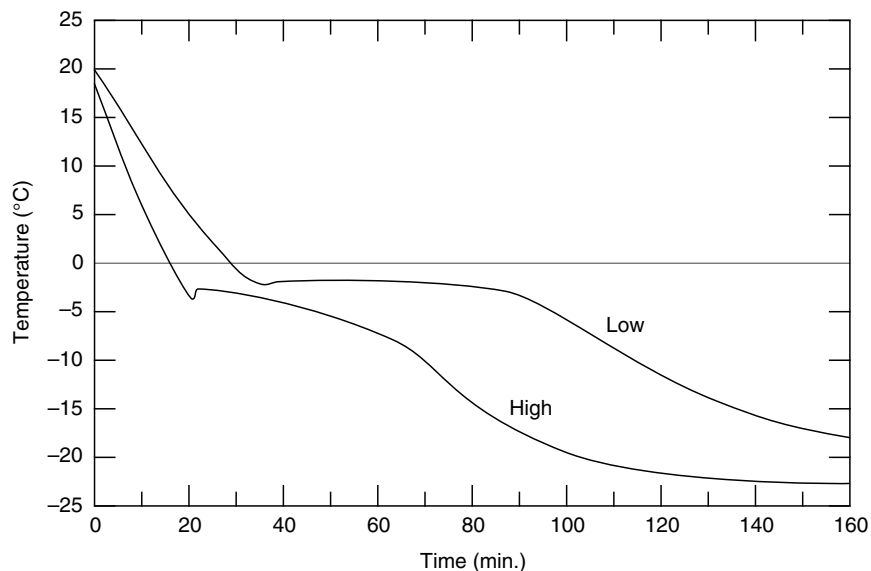
Despite the apparent problems with the temperature of the room, the useful conclusion from these tests was that the accelerator doses could be much higher than those recommended by the manufacturer, especially in cold weather.

The freezing points were determined by embedding thermocouples into cylinders of fresh mortar placed into a -20°C (-2°F) room. Figure 1 shows how the temperature changes as thermal energy is extracted from control mortar on the one hand, and from mortars con-

taining two doses of accelerating admixture on the other. In general, the three curves show that mortar steadily cools from room temperature to the point where ice suddenly appears. This event is easily identified on all three curves as the location where the initial slope changes. However, a close inspection of each curve reveals that there are two temperatures to choose from at this juncture. For example, the control mortar gradually cooled from 22°C (71.6°F) to -2.3°C (27.9°F) before suddenly rising to -1.9°C (28.6°F) and holding there for many hours. The lower of the two temperatures represents the instant at which ice spontaneously



a. Control mortar.



b. Two mortars made with a low and high dose of ASTM Type C accelerator.

Figure 1. Cooling curves.

nucleated while the higher temperature, and the one that defines the freezing point, is where ice grows. As heat is removed from the water, just enough of the water turns into ice to replace it as heat of fusion and, thus, the temperature remains constant until all of the water solidifies. At that instant the temperature begins to drop again until it reaches ambient.

Strictly speaking, solutions, such as the mixing waters in each mortar in Figure 1, should not freeze at a single temperature. The solid that freezes from a solution is pure H₂O or ice. As ice grows, the concentration of alkalis and other additives in the remaining liquid increases. Progressively lower temperatures are required if more ice is to grow. However, the constancy of the temperature of the control and the mortar containing the low dose of accelerator suggests that, for practical purposes, these two mixes have only one freezing temperature. The mortar made with the higher concentration of admixture (high dose curve, Fig. 1b) exhibits the expected progression of freezing points whereby the temperature does not hold constant but continues to fall over time. The main finding from these tests, however, was that none of the admixtures when used alone and when added to mortar in permissible amounts lowered freezing points significantly (Table 3).

Combining the admixtures

Standard practice places no limit on the number of admixtures that can be used in concrete, just on individual amounts. The objective, therefore, was to use as many admixtures as needed to develop a mortar that

would set faster than the control at room temperature and that would resist freezing and gain significant strength at -5°C (23°F) or below. Since the successful admixture combination would have to accelerate cement hydration at low temperature and protect the water from freezing, the approach was to combine accelerators with water reducers while maintaining workability (flow). Table 4 shows how the admixtures were combined and how they affected the mortar compared to the control (mix 1).

The first step evaluated the freezing point depression and accelerated cure properties of the Type E accelerating admixture combined singly with the Type A and F water reducers to produce mixes 2 through 4. Mix 2 used the Type E accelerating admixture at 67 percent of its recommended dose with the Type A water-reducing admixture at 100 percent of its recommended dose. As Table 4 shows, the water-reducing capability of these two admixtures permitted the w/c ratio to be lowered from 0.48 of the control to 0.41 with the result that the freezing point dropped from -1.9°C (28.6°F) of the control to -3.4°C (25.9°F). This combination of admixtures, however, did not satisfy the need for a -5°C (23°F) freeze protection or for an initial set time of less than 3.2 hours—mix 2's set time was 7.25 hours. To speed up hydration and add more solutes into the mix water, the Type E admixture was increased to full dose with the Type A admixture, also at full dose. This change dropped the freezing point to -3.9°C (25°F) but the initial set increased to 8.25 hours. Mix 4 replaced the Type A admixture with Type F and combined it with the Type E admixture, both at full

Table 4. Properties of fresh mortar made with admixture combinations. Set times and flow were conducted at 19°C while freezing points were obtained at -20°C . The letters in column 2 correspond to admixtures of Table 1. Water contents were changed in all but mixes 8 and 9 to keep flow constant.

Mix no.	Mortar designation	Initial set (hr)	Final set (hr)	Freezing point ($^{\circ}\text{C}$)	Flow (%)	w/c ratio
1	Control	3.2	4.4	-1.9	104	0.48
2	E(67*) + A(100*)	7.25	na	-3.4	103	0.41
3	E(100) + A(100)	8.25	10.3	-3.9	103	0.39
4	E(100) + F(100)	6.1	na	-4.0	102	0.37
5	C(100) + D(625)	8.25	9.5	-3.1	101	0.39
6	C(200) + D(625)	5.1	7	-4.0	103	0.38
7	C(100) + E(100) + F(100)	4.9	6.5	-4.9	107	0.39
8	C(100) + E(100) + F(100)	na	na	-5.7	too dry	0.30
9	C(100) + E(100) + F(100) + 2% CaCl_2	na	na	-9.2	set too fast	0.34

*Percent of maximum dose recommended by the manufacturer.

dose. This change dropped the freezing point to -4.0°C (24.8°F) and the initial set to 6.1 hours.

It was apparent from mixes 2–4 that more admixtures were needed to depress the freezing point further. To do this, mixes 5 and 6 used the Type D, water-reducing and retarding admixture at 6.25 times its maximum dose and the Type C accelerator at both full and twice-normal dose. Though these mixes used admixtures at higher than normal, it was hoped that they would provide an indication of how much admixture would ultimately be needed. As Table 4 shows, the retarding effect of the Type D admixture when used with the Type C accelerator at full dose caused mix 5 to set at 8.25 hours and to freeze at -3.1°C (26.4°F). Mix 6 counteracted the slow setting of mix 5 by doubling the quantity of the Type C admixture. As can be seen, mix 6 set at 5.1 hours and froze at -4.0°C (24.8°F). The accelerator seemed to help but, obviously, more was needed.

To attain these higher concentrations while staying within recommended levels, mix 7 used both the Type C and E admixtures at 100 percent of their recommended doses and combined them with the Type F water reducer, also at 100 percent of its recommended dose. This combination nearly produced the sought-after admixture as it set at 4.9 hours and froze at -4.9°C (23.2°F). In addition, Table 4 shows that the flow of 107 percent was a bit higher than that of the control. This suggested that the w/c ratio of this mix could be reduced, which would, in effect, cause the admixture concentration in the mix water to increase and the freezing point of the mortar to decrease. Mix 8 tried this approach by reducing the w/c ratio to 0.30 while keeping the admixtures the same as those in mix 7. Table 4 shows that this mix achieved a freezing point of -5.7°C (21.7°F). Unfortunately, it was too dry to be practical.

Mix 9 combined the two commercial admixtures with calcium chloride, each at their maximum allowable dosage, with the Type F high-range water reducer. This produced an initially workable mix with a -9.2°C (15.4°F) freezing point. However, it set up during the casting of strength specimens (within half an hour of water hitting the cement) so that setting times could not be measured. Time did not allow additional testing.

Strength gain

The mixes shown in Table 4 were tested for strength gain at four temperatures. Table 5 shows those results. Although the ones of most interest are mixes 8 and 9 (because they had freezing points that were below the -5°C [23°F] target set at the beginning of this study), all strength results are given. The results from mixes 2–7 will not be discussed except to note that mixes 4 and 5 achieved very low strengths, even at room temperature. It is not clear why this happened.

What is clear is that both mixes 8 and 9 performed well at -5°C (23°F). They gained strength more rapidly at that temperature than control mortar cured at 5°C (41°F). The 5°C (41°F) represents the lowest temperature at which concrete currently can be cured (ACI 1988). Concrete (mortar) usually gains 30, 56, and 83 percent of its 28-day room temperature strength when cured for 7, 14, and 28 days, respectively, at 5°C (41°F). With this as guidance, it can be seen that mixes 8 and 9 performed well down to -10°C (14°F), even though neither possessed a freezing point that low. It appears that a mix must have a freezing point of at least -5°C (23°F) to perform well, as those with -4.0°C (24.8°F) freezing points did not do well at even -5°C (23°F). Interestingly, both mixes, though they gained little strength, recovered full strength after being cooled to -20°C (-2°F).

CONCLUSIONS

This study showed that admixtures used in today's concrete could be combined to allow fresh concrete to gain appreciable strength at below-freezing temperatures. Freezing points as low as -9.2°C (15.4°F) were developed by combining a Type C, a Type E, and a Type F admixture along with calcium chloride, all within allowable doses. This combination of admixtures produced higher strength in mortar cured at -5°C (23°F) for 14 days than did control mortar cured for the same time at 20°C (68°F). What is more, this admixture combination produced significant strength in mortar cured at -10°C (14°F) and allowed mortar to recover full strength when thawed after being at -20°C (-2°C). The problem with this admixture combination was that it caused the mortar to set too rapidly.

Additional work should be done to find the combination(s) of off-the-shelf admixtures that permit concreting to -10°C (14°F) without setting too rapidly. Though all admixtures conforming to ASTM C 494 (ASTM 1997c) have individually passed a battery of tests to prove that they cause no harm to the concrete, little is known on how they react when used in combination with other admixtures or with admixtures from other companies. Thus, admixtures in various combinations and from various sources should be studied for their affects on concrete and embedded metal. For example, preliminary data suggest that high doses of admixtures can sometimes improve the resistance of concrete to cycles of freezing and thawing. It is not recommended that the results of this study be applied directly to field application until additional study and testing are done.

Future work should focus not only on portland

Table 5. Strength gain of mortar cured at various temperatures for 14 days, then at 20°C for 21 days.

20°C				-5°C			
Mix	Days			Mix	Days		
	7	14	35		7	14	35
1	80.1	91.6	100.0	1	7.3	10.8	45.0
2	64.1	66.0	74.3	2	26.5	33.4	47.0
3	82.5	91.0	101.4	3	31.3	49.2	75.5
4	2.0	2.3	3.0	4	2.7	2.7	3.4
5	3.8	4.2	95.3	5	1.3	1.7	2.8
6	60.5	63.4	71.7	6	32.2	39.2	68.8
7	55.8	62.2	79.8	7	32.2	45.5	68.5
8	100.3	116.1	130.8	8	73.1	76.3	128.2
9	136.2	149.1	166.8	9	78.8	101.8	172.2

-10°C				-20°C			
Mix	Days			Mix	Days		
	7	14	35		7	14	35
1	1.7	2.9	41.9	1	0.0	0.6	68.0
2	16.4	22.4	39.7	2	0.0	0.0	62.0
3	15.6	27.4	58.4	3	0.0	0.2	82.6
4	0.0	0.6	3.7	4	0.0	0.0	4.1
5	1.1	1.6	3.4	5	0.5	0.5	6.8
6	16.3	18.5	45.7	6	0.5	0.7	51.2
7	11.4	18.8	40.3	7	1.7	2.5	45.7
8	32.2	47.6	111.8	8	5.0	6.7	116.0
9	28.0	55.5	155.6	9	4.4	7.3	151.9

cements, but on other cements as well. Appendix A provides insight into other types of cements.

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APPENDIX A: ALTERNATIVE CEMENTS

Asok Sarkar, formerly of the University of Dayton Research Institute, provided this analysis of cements other than plain portland cement for potential use in cold weather. This is not intended to be an exhaustive review but rather to serve as an introduction to alternative cements.

A considerable amount of effort has been expended both in northern America and Europe to devise ways by which construction can continue throughout the winter season. In general, North American concreting practices have tended towards the use of heating and housing to protect fresh concrete during placement and curing. However, in view of the cost and logistical problems associated with transporting the equipment needed for heating and housing, there is a significant need for concreting and repair materials that can function without elaborate costly protection measures.

Cementitious binder materials can be classified into three broad categories: 1) inorganic cements, 2) organic polymer resins, and 3) hybrid inorganic-organic binders. The useful temperature range of regular and blended portland cements can be extended by the use of various accelerators, antifreezing agents, and combinations thereof. Several inorganic non-portland cements have also been used for cold weather applications. For any cement material to perform effectively at low temperatures, several key properties—such as rapid setting, rapid strength gain, and self-generation of heat—are needed.

INORGANIC CEMENTS

For inorganic cements to function at low temperature, the mix water must remain liquid during both mixing and initial hydration.

Portland cement

The main concerns for cold weather concreting with portland cement are maintaining an adequate temperature for curing the concrete and protecting the concrete from both freezing and large thermal shocks. There are two ways to overcome the low-temperature limitations of portland cements: accelerating the setting and hydration reaction of the cement, and depressing the freezing point of the free water in the cement matrix. Both of these aspects have been discussed in the main body of this report. More research with novel additives and admixtures is required in this area.

Supplementary and blended cements

Blended cements are made of mixtures of regular Type I portland cement with various siliceous supplementary cementing materials, for example, blast furnace slag, fly ash, silica fume, and natural and artificial pozzolans. Besides providing significant cost reduction of the placed concrete, these replacement materials can act to improve workability; reduce water/cement ratio; reduce porosity of the concrete; lead to improved durability; and can reduce the heat of hydration of cement, leading to lower thermal stresses in large concrete structures. While the reduced heat of hydration of blended cements is advantageous for the construction of large concrete structures, it is a serious drawback for the construction of smaller structures at low temperatures. For this reason, blended cements are not normally selected for use at low temperatures unless heating and housing are available. Work is needed to find chemicals that will speed up the normally slow hydration reaction of supplementary cementing materials.

Modified portland cements

Modified portland cements are often manufactured because of raw material constraints, and several have been formulated and produced specifically for low energy consumption

during production. Many that were developed in east Europe generally suffer from low strength-gain characteristics. Thus, they are not expected to be good candidates for low-temperature cements.

However, other fast-setting and very high early strength portland-cement-based binders have been manufactured that have very good potential for low-temperature applications. The basic matrix of these modified cements are portland cements that contain additional phases which can react with water very rapidly, causing an early onset of setting and hardening. These cements are usually manufactured from a single homogeneous clinker or can be produced by intergrinding and/or blending special clinkers and additives with regular portland cement clinkers. Since they are special cements and are not used routinely, they are generally two to three times more expensive than regular portland cement. Important physicochemical properties of these cements are described below.

Regulated-set or Jet cements

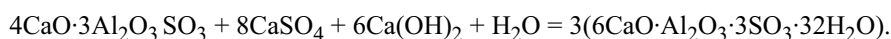
Regulated-set cement, also called Jet cement in Japan, is manufactured under patents issued to the U.S. Portland Cement Association. A modified portland cement clinker containing mainly alite (tricalcium silicate, C_3S) and a calcium fluoroaluminate ($11 CaO \cdot 7 Al_2O_3 \cdot CaF_2$) is made. A suitable proportion of the fluoroaluminate clinker is blended with normal portland cement clinker and calcium sulfate so that the final cement contains about 20 to 25 percent of the fluoroaluminate compound and about 10 to 15 percent calcium sulfate. The cement is generally very fast setting at room temperature, but can be retarded to the desired set time by using citric acid, sodium sulfate, calcium hydroxide, boric acid, and other retarders. A chloride analog of this cement was also made in the Soviet Union. However, since the presence of chloride ions was found to induce corrosion in the steel reinforcements, this cement has not enjoyed much popularity.

The basic hydration reactions of the silicates present in this cement are the same as for regular portland cement. However, the hydration of the fluoroaluminate, which is responsible for the rapid-setting characteristics of Jet cement, is extremely complex, and is further complicated by the presence of other set-regulating compounds that are added to achieve reasonable working time. The early strength development of regulated-set cement is due to the rapid reaction of the haloaluminate phase with calcium sulfate forming ettringite. The ultimate strength and other physical properties of this cement are comparable to those of the portland cement except that, because of the high content of the reactive aluminate phase, the sulfate resistance of structures made with these cements will be poor.

Regulated-set cement is very popular in Japan and is quite frequently used for winter constructions and repairs at ambient temperatures of -3° to $-5^\circ C$ (27° to $23^\circ F$), although the curing operation is facilitated by covering the constructed surfaces with canvas sheets.

Sulfoaluminate cement

The formation of large quantities of ettringite is responsible for the properties of sulfoaluminate-phase-containing cement, also known as the very high early (VHE) strength cement. The VHE or the sulfoaluminate cement is commercially available (manufactured) in the United States. In contrast to the expansive Type K cements, the formation of ettringite when these cements come in contact with water gives rise to rapid strength development. The processing science of these cements has improved quite rapidly in recent years. Minor expansions that were often experienced earlier with these cements have been controlled to the point that these cements are sold as zero-shrinkage cements. In these cements, like the haloaluminate cement, the ettringite formation is very rapid, occurring largely before the paste has gained strength and well before hydration of the calcium silicates. The ettringite formation reaction for this cement can be written as



This cement is being marketed for special use and has limited use at low temperatures.

For this reason, the low-temperature properties of these phases or blended cements have not been thoroughly studied. Moreover, because of limited use, large cement producers do not usually market these special cements. On the other hand, companies who sell these materials are very secretive about releasing any data on the cements except strength.

High iron cements

Just like the previous two modified portland cements, the high iron cements derive their rapid setting and hardening characteristics from the formation of large amounts of ettringite during the early hydration period. However, unlike the VHE cement, both sulfoaluminate (C_4A_3S) and C_4AF phases provide the aluminate ions. This cement is still under development and may have considerable appeal to the construction industry again, perhaps for economic reasons.

Pyrament cement

Pyrament was the trade name given to a blended hydraulic cement product manufactured by Pyrament, Inc., of Houston, Texas. This cement was the result of a new invention by the company and was marketed as cement compositions curable at low temperatures. It was claimed that by employing the formulation of the invention, contrary to using existing cements, cures could be effected at temperatures well below the freezing point of water and, in fact, cure could be accomplished at temperatures as low as -16°F (3.2°F).

This cement is composed of portland cement, slag, pozzolans including metakaolin, and admixtures including potassium carbonate and water-reducing agents. Use of potassium carbonate with the metakaolin is required to ensure continuing cure of the cement at temperatures below the freezing point of water.

Calcium aluminate cement

Compared to portland cement, calcium aluminate cement (CAC) possesses many unique properties, such as high early strength, hardening even under low-temperature conditions, and superior durability to sulfate attack. However, CAC is not recommended for structural use because the hardened cement can experience gradual strength retrogression. Therefore, in most countries, CAC is now used mainly for making castable refractory linings for high-temperature furnaces. However, since the cement has some desirable characteristics, further examination of its properties has been advocated.

CAC is the product obtained by pulverizing calcium aluminate cement clinker manufactured by partially or completely fusing calcareous materials, such as limestone or chalk, and an alumina source, such as bauxite, to convert them to hydraulic calcium aluminates. This is the reason why in France and Germany the cement is called *ciment fondu* and *tonerdeschmelz zement*, respectively. Thus, unlike portland and modified portland cements, in which di- and tricalcium silicates are the principle cementing compounds, in CAC the monocalcium aluminate (CA) is the principal cementing compound, with $C_{12}A_7$, CA_2 , C_2AS , β - C_2S , and F_{ss} (iron solid solution) as minor compounds. Typically, the chemical analysis of ordinary CAC corresponds to approximately 40 wt% Al_2O_3 , and some cements contain even higher alumina content (50 to 80 wt%). For these high alumina contents, CAC is also referred to as high-alumina cement (HAC).

The bauxite ore used to produce CAC contains a considerable amount of iron as an impurity, which accounts for the 10 to 17 percent iron (expressed as Fe_2O_3) usually present in ordinary CAC. This is why, unlike portland cement clinker, the CAC clinker containing high iron is in the form of completely fused melts that are made in specially designed furnaces. On the other hand, cements meant for high-temperature applications containing very low iron and silica are made by sintering in rotary kilns.

Although CAC materials have setting times comparable to ordinary portland cement, the rate of strength gain at early ages is quite high, mainly due to the high reactivity of CA. Within 24 hours of hydration, the strength of normally cured CAC concrete can attain values equal to or exceeding the seven-day strength of ordinary portland cement. Also, the

strength-gain characteristics under subzero curing conditions are much better than for portland cements. CAC has been used successfully in the past for cold weather construction, and in fact manufacturers of CAC provide data sheets promoting its use at temperatures below -3°C (27°F), and claim successful results at temperatures as low as -40°C (-38°F). It may be noted that the heat liberation rate of freshly hydrated CAC can be as high as 9 cal/g per hour, which is about three times as high as the rate for high-early-strength portland cements. Although CAC does not set faster than portland cement, it does develop strength and evolve heat at a much faster rate after the initial set has commenced. After 24 hours, the strength of CAC concrete can reach 90% of its ultimate strength, and its rapid strength gain is accompanied by rapid evolution of heat. For this reason, CAC, after initial setting, can tolerate much colder ambient conditions than its portland cement counterpart. However, CAC concrete must be protected from freezing, in much the same way as portland cement concrete, until setting and some strength development has occurred.

CAC hydration can also be accelerated like portland cement by the addition of small quantities (~ 0.5 wt% of the water) of various compounds. Among many candidates, LiCl has been reported to produce the greatest effect. In terms of decreasing effectiveness, the cations have been found to follow the order $\text{Li} \ll \text{Na} < \text{none} < \text{K} < \text{Ca} < \text{Mg} < \text{Sr} < \text{NH}_4$, while the anions follow the order $\text{OH} \ll \text{none} \ll \text{Cl} < \text{NO}_3 < \text{Br} < \text{acetate}$. Hydroxy compounds, such as sodium and calcium hydroxide, generally accelerate the CAC hydration, whereas both magnesium and barium hydroxides have been found to act as retarders. Citric acid is the most common retarder for the system, although glycols, glycerine, sugars, casein, and chloride salts such as NaCl, KCl, CaCl_2 , and MgCl_2 can also work as retarders.

It has been found also that up to 20 wt% portland cement addition to CAC accelerates its set reaction, and at the same time, small quantities of CAC act as set accelerators for the portland cement. Various proprietary formulations based on the mixture of portland cement and CAC have been marketed, and preliminary research work conducted on these combinations has shown that the acceleration effect of CAC on portland cement, and vice-versa, is variable and depends strongly on the type and source of the CAC. Therefore, prior trial runs should be done before any combination is used for field applications. It was also found that when *fondur* cement was accelerated with lithium carbonate, it performed well in terms of strength development on small-size specimens; however, on larger-size specimens, the strength development was very poor at room temperature, probably because of the large amount of heat generation, which might have altered the nature and morphology of the crystalline calcium aluminate hydrates.

Currently, the major use of CAC is as refractory cements where chemical bonds develop at high temperature, obliterating the effect of any conversion reactions. However, for use under cold weather conditions, CAC seems to possess many of the required properties, although the deleterious strength retrogression during service in warmer climates must be taken into consideration before the concrete is designed for a particular job.

Calcium-sulfate (gypsum) cement

Crystallization of gypsum needles from a hydrated gypsum cement is the cause of setting and hardening that has been exploited by the wallboard industry. However, gypsum is not stable in water and therefore gypsum cement is nonhydraulic. Because of this poor moisture resistance, its use has been mainly reserved for indoor applications.

Although unmodified gypsum cements have restricted use, the material CaSO_4 has been used as additives in many cement blends and formulations for both portland cements and CAC to produce cement formulations for low-temperature applications.

Magnesium phosphate cement

If fast-setting and cold-weather characteristics are required simultaneously, then the most cost-effective alternative are the phosphate cements based on MgO –ammonium phosphate–water chemistry. These cements are not compatible with regular portland cement. Laboratory tests have been performed to show that these cements can be formulated to set up

within one hour (2- \leftrightarrow 2-inch specimen) at temperatures of -20°C (-2°F), when the surfaces are protected from quick heat loss by covering with regular polymeric materials. Areas that need further exploration are exothermic heat control, improving hydraulicity, and freeze-thaw durability.

Magnesia cements

There are magnesium-oxide-based cements known as magnesium oxychloride and oxysulfate cements. These cements have very poor stability in moist environments and therefore have not enjoyed much widespread use for outdoor applications.

Sulfur cement

Commercial development of sulfur concrete started in the 1970s in order to find potential markets for elemental sulfur. The sulfur concrete consists of elemental sulfur, sulfur polymer stabilizer, fine filler material, and aggregates. Mix proportioning is accomplished using a suitable dense-graded aggregate in combination with sulfur and filler to provide good workability for the application. Sulfur concrete is produced by a hot mix procedure similar in some respects to that of asphalt.

Sulfur concrete is a construction material with unique properties and characteristics. It performs very well in many aggressive environments and offers many benefits as an alternative construction material, particularly in situations that require a fast setting time, placement in excessive cold or hot climates, corrosion resistance, and impermeability.

ORGANIC POLYMER RESINS

Many polymeric systems can be used to prepare polymer mortar and concrete by completely replacing the cement hydrate binders of conventional mortar and concrete with polymeric binders. A wide range of aggregates and monomers can be used, although the cost and properties of the polymer concrete are strongly influenced by the gradation and monomer. A well-graded aggregate may require as little as 5 to 8% monomer by weight, while more than 15% may be required for gap-graded aggregate. Most of the thermosetting resin and monomer systems for the polymer mortar and concrete are polymerized at ambient temperatures, which can vary from normal weather to cold weather.

In polymeric cement systems, the cement hydrate binders of conventional mortar and concrete are replaced with polymeric binders, and the aggregates that are the same as the conventional products are strongly bound to each other by the uniform polymer matrix phases obtained from the polymeric binders. Accordingly, compared to ordinary cementitious materials, properties such as strength, adhesion, water-tightness, chemical resistance, freeze-thaw durability, and abrasion resistance of polymeric cement systems are generally improved to a great extent by polymer replacement. On the other hand, the poor thermal and fire resistance and large temperature dependence of mechanical properties are some drawbacks caused by the undesirable properties of the polymer matrix phases.

The processing technology of polymeric cement systems is the same as that of the conventional cement systems, so that the batching, mixing, and placing techniques for regular cement products are applicable for polymeric systems. However, the curing methods are different. The optimum cures, such as dry cure at ambient temperature or heat cure, are applied to polymeric cement systems. Generally, the process technology of the polymer systems is divided into two categories: cast-in-place and precast application systems. At present, the cast-in-place application systems are chiefly applied for the polymer mortar, and the precast application systems are used for the polymer concrete. In order to reduce the cost of polymer mortar and concrete systems, it is very important to find out the effective mix proportions of the polymeric binders and the aggregates. Any of the polymeric binders are toxic and flammable and therefore the established safety procedures should be strictly followed.

A variety of polymeric binders to produce mortar and concrete are commercially available. These include various thermosetting resins, tar-modified resins, resin-modified asphalts, and vinyl monomers. Different kinds of binders are popular in different countries; these are dictated mostly by availability and cost. For example, in Japan, the binders for polymer mortar are chiefly epoxy resins, unsaturated polyester resin, such as polyester-styrene systems, vinyl ester resin, and methyl methacrylate monomer whereas, for the polymer concrete products, the common binder is unsaturated polyester resins. On the other hand, the most common polymeric binder types in the United States and western Europe are methyl methacrylate monomer, unsaturated polyester, and epoxy resins, among which the unsaturated polyester resin has the lowest cost. Furan resin, mainly the furfural-acetone resin, is widely used in the former Soviet Union and east European countries. In addition to these conventional manufactured synthetic resins, application of recycled monomers and polymers to the synthetic binders has also been made recently.

Polymeric binders cannot set or harden by themselves, and for this reason various initiators, promoters, and hardeners are selected and added to the polymeric binders at the time of mixing the mortar and concrete. As mentioned earlier, polymeric binder systems are quite different from the ordinary hydraulic cement systems; like their regular cement counterpart, there are various guidelines published by the American Concrete Institute for the use of polymer concretes.

Unsaturated polyester and vinyl ester resins

Unsaturated polyesters are condensation polymers formed by the reaction of polyols and polycarboxylic acids with olefinic unsaturation being contributed by one of the reactants, usually the acid. The polyols and polycarboxylic acids used are usually difunctional alcohols (glycols) and difunctional acids such as phthalic and maleic. Water is produced as the by-product of esterification reaction and is removed from the reaction to drive the polyesterification reaction to completion. All of the materials used must be at least difunctional to make the polyesterification reaction possible.

Unsaturated polyesters copolymerize with monomers having olefinic unsaturation much more rapidly than they homopolymerize, so most unsaturated polyesters are used as mixtures with reactive, usually liquid, monomers. Of such monomers, styrene is by far the most used monomer. Styrene used in polyester resins is low in cost, provides low-viscosity resins at reasonable monomer levels, and copolymerizes readily with unsaturated polyester alkyd at various temperatures. Laboratory tests indicate that for optimum workability, the styrene content is 45 to 50% of the resin content, although styrene content as low as 35 wt% has been used. The copolymerization chemistry of unsaturated polyester alkyds and unsaturated monomers is usually initiated by free radicals generated by the decomposition of peroxides, azo compounds, or free radicals generated by the use of medium- to high-energy radiation, such as ultraviolet light or electron beams. Commercially, visible-light-cure polyesters are also available and the curing occurs independently of ambient conditions. Microwave curing of polyester resins has also been demonstrated.

Commercial polyester resins have been demonstrated to be useful at curing temperatures as low as -10°C (14°F) without many handling difficulties. Polyester-styrene concrete products have several advantages for the rehabilitation of portland cement concrete. They are highly abrasion-resistant and impermeable to water and road salts, and are effective in thin layers ranging from 3/8 to 1 inch thick, thereby reducing dead load and clearance problems. They are well suited to night work in heavy traffic areas where bridge or road closures must be kept as brief as possible. The resins to produce the concrete are relatively inexpensive and are readily available. The vinyl esters also are available as grouts or toppings for concrete repair, although their curing properties sometimes limit their use to applications above 10°C (50°F). There is one concern with the polyester concrete: research has shown that the compressive strength of polyester concrete decreases as temperature increases, and thus the durability may be a problem under cycling temperatures.

Epoxy resins

Chemically, an epoxy resin contains more than one α -epoxy group situated terminally, cyclically, or internally in a molecule that can be converted to a solid through a thermosetting reaction. The conversion of epoxy resins from the thermoplastic state to tough, hard, thermoset solids can occur via a variety of crosslinking mechanisms. Epoxies can catalytically homopolymerize or form a heteropolymer by coreacting through their functional epoxide groups with different curatives. In epoxide technology, curatives are most frequently called curing agents. Often, the terms hardener, activator, or catalyst are applied to specific types of curing agents. For most commercial products, the curing agents' chemical structure is kept proprietary, or the amount of reactive functional group is ambiguous. Epoxy curing agents can be divided into two major classes: alkaline and acidic. The alkaline class includes Lewis bases (tertiary amines), primary and secondary amines and amides, and other nitrogen-containing compounds. The acidic class of epoxy curing agents includes Lewis acids (metal halides such as zinc, aluminum, and ferric), phenols, organic acids, carboxylic acid anhydrides, and thiols.

The properties of epoxy resins can vary over a wide range, depending on the selection of a formulation's ingredients, their relative proportions, the processing of the formula, and the configuration and environment of the final product. Some generalization about epoxy resin properties are possible. Epoxy resins, toppings, and patching materials may be used for the repair of cracks, spalls, joints, and other problem areas. Epoxies generally cure within 8 to 12 hours at ambient conditions of 21°C (70°F). Liquid resins and curatives can form low-viscosity, easily modified systems. They can cure at temperatures from -40°C (-40°F) to 200°C (392°F), depending on the curing agents used. They exhibit very low shrinkage and do not evolve volatile by-products during cure. Commercially, various kinds of modified low-temperature formulations are available, some of which can be quite applicable for cold-weather applications.

Furan polymers

The term furan polymer or resin is a loosely defined term. It can be used to denote polymers based on furfural, furfuryl alcohol, or furan. Furfural is the starting material for all of these compounds. The chemical resistance of furan resins has been used for many years to advantage in chemical cements. Urea-formaldehyde-furfuryl alcohol resins for foundry usage constitute the largest market for furans. This cement system has very good potential for low-temperature applications.

Furan resins potentially provide the following important advantages: 1) low cost; the fact that they do not require petroleum-based feedstock should enhance the cost/availability outlook for these resins; 2) rapid cure and low-temperature cure; 3) extended shelf life. The uncatalyzed furan resins have virtually unlimited shelf life. Furan resins (mainly furfural-acetone resin) are widely used in the Soviet Union (now Commonwealth of Independent States) and eastern Europe. The furan resin systems are often acid-catalyzed; because of this, sometimes the bonding with alkaline portland cement systems has been found to be a problem. The most popular resin used in European countries is formed using a ratio of 1.5:1 furfural to acetone, the main components of which are monofurfurylidenacetone, difurfurylidenacetone, and furfural. Different percentages of these components in the various resins greatly influence the polymerization mechanism, causing noticeable variances in the properties of the material. The most popular hardener for furfural acetone resins is benzosulfoacid; *n*-toluosulfochloride and toluosulfoacid are also commonly used. Chloride compounds of iron, concentrated sulfuric acid, and amine hardeners are also sometimes used.

A furfuryl-alcohol-based polymer has been developed for achieving high early strength at ambient temperatures of 52° to -32°C (125° to -25°F). The polymerization of the furfuryl alcohol was controlled by using a unique combination of α , α , α -trichlorotoluene (TCT) catalyst, and zinc chloride promoter in conjunction with a pyridine retarder. The working time for the polymer slurry can be controlled at >15 minutes over the entire tem-

perature range by simply varying the TCT catalyst concentration while holding all of the other constituents constant.

Polyurethanes

Technically, polyurethanes are the reaction products of molecules containing two or more isocyanate groups (polyisocyanates) with molecules containing two or more hydroxyl groups (glycols, polyols, glycerine, etc.) and water and phenols, to form the chain, making a series of interconnected isocyanates and hydroxy-containing molecules. Since the configurations of the ingredients can be varied to produce macromolecular polyurethanes, many different types of polyurethane chains and spatial configurations can be designed for any specific purposes, with one's curiosity limited only by one's imagination. However, the commercial availability of raw materials and toxicity problems may limit the free design of molecular structures.

Polyurethanes are commonly used for concrete sealing during new construction periods. Chemical grouts are also available for nonstructural crack repairs. Polyurethanes are generally applied at temperatures above 4°C (40°F), with cure achieved within 24 to 72 hours. However, several specially formulated polyurethanes have been commercially available that have the potential for low-temperature use. A commercial urethane resin system known as EP system (manufactured by Ashland Chemical Co., Columbus, Ohio 43216) can be cured at temperatures as low as -30°C (-20°F) as a neat solution or mixed with sand, while maintaining low viscosity and good workability for cast-in-place construction without adding any heat or protection from freezing.

Phenolic resins

Phenolic resins are the reaction product of one or more of the phenols with one or more of the aldehydes. The use of substituted phenols and the aldehydes other than formaldehyde is very limited. Resins based on resorcinol can be cured at room temperature. Among the aldehydes, furfural is the only one in commercial use other than the various forms of formaldehyde. The presence of furfural makes the cured resin softer. Also, furfuryl alcohol can be mixed with the resin to reduce the viscosity of the mix and allow higher filler ratio. Commercial phenolic resin-based concretes made with BP Chemical J50/010L with acid catalyst Phencat 15 and Foduth Chemical IR 1271 with acid catalyst CS 30 can be cured at room temperature with higher levels of the catalyst. For lower catalyst amount, application of pressure and heat may be required.

Phenolic concretes are claimed to possess equivalent mechanical properties and superior fire and chemical resistance to all other types of resin concrete developed to date. They are high-temperature performance materials, have good resistance to corrosion and microbiological attack, do not absorb water, and have high resistance to attack by a range of common chemicals. Phenolics are affected by alkalis and by oxidizing acids. They are resistant to weak acids, solvents, detergents, and hydrocarbons. Extended exposure to weathering and UV can cause failure.

Phenolic concrete is tougher and stiffer than ordinary concrete and is usually as tough as polyester concrete. The level of the acid catalyst that can be successfully used in phenolic concrete has been shown to be determined by the mix and casting process, type of catalyst, and temperature. No cold weather use has been found for phenolic concrete.

Acrylics

Acrylic and methacrylic acid and their esters are included in the acrylic group. However, the most important plastic in the family of acrylic resins is polymethyl methacrylate (PMMA), a colorless transparent plastic with a higher softening point, better impact strength, and considerably better outdoor weathering properties than polystyrene.

PMMA has received the attention of most of the work in polymer concrete development in the United States in the last several years, especially for the repair of concrete. Benzoyl peroxide is the most commonly used initiator, and N,N-dimethylparatoluidine and dim-

ethyl aniline are widely used promoters for this system. A multifunctional monomer known as trimethylol propane trimethacrylate is also used in combination with the methyl methacrylate in 5:95 ratio to increase the rate of polymerization of the acrylic system. The promoter and initiator content can be adjusted to control the setting time at any given temperature, thus making this system usable for cold-weather patching at low temperatures. Methacrylate systems (Degussa Corporation, Ridgefield, New Jersey) are able to cure fully in one to two hours at temperatures down to -29°C (-20°F) and are generally utilized for resurfacing, patching, and joint rehabilitation.

This system has been successfully lab-tested at temperatures between -9.4 to -6.7°C (15 to 20°F). However, the performance of commercial systems at low temperatures needs further investigation since no successful outside patching at low temperatures has been reported. Also, the requirement for dry aggregates and patch surfaces and strong odor are several handicaps of this system.

HYBRID INORGANIC-ORGANIC BINDERS

Two kinds of materials, polymer- (latex) modified and polymer-infiltrated binders, fall under this category. In recent years, polymer latex-modified mortars and concrete have been widely used as construction materials because of their improved properties of high strength, extensibility, adhesion, waterproofing, and durability. Three kinds of latexes have been used for this purpose. The most common latex has been the styrene-butadiene copolymer. Other latexes, such as vinylidene chloride-vinyl chloride copolymer and polyacrylic esters, have also been used for mortar applications. Generally, latex-modified concrete will provide higher strength after air curing compared to water curing because of the film-forming ability of dried latex particles. However, no use of such binders at low temperatures was found in the literature. One problem with these latex suspensions is that they should not freeze, because the suspension property would be lost and the latex particles would not be uniformly distributed throughout the matrix.

The polymer-infiltrated concrete has been primarily used for restoration purposes. The acrylic polymeric systems described previously under the organic binders can be used for this purpose. The low viscosity of acrylic monomers helps the infiltration of the monomer within the matrix. Because acrylics can be used at low temperatures, repair and restoration of damaged concrete can be performed applying this technique.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YY) January 2001		2. REPORT TYPE Technical Report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Off-the-Shelf Antifreeze Admixture for Concrete: Initial Laboratory Investigation				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Charles J. Korhonen and Sherri A. Orchino				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Research and Development Center Cold Regions Research and Engineering Laboratory 72 Lyme Road Hanover, New Hampshire 03755-1290				8. PERFORMING ORGANIZATION REPORT NUMBER ERDC/CRREL TR-01-2	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR / MONITOR'S ACRONYM(S)	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. Available from NTIS, Springfield, Virginia 22161.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Set-controlling and water-reducing admixtures conforming to ASTM C 494 were studied for their effect on strength gain of portland cement concrete at below-freezing temperatures. Because standard practice does not limit the number of admixtures that can be used in concrete, the objective was to use as many admixtures as necessary to depress the freezing point of the mix water to -5°C (23°F) or below and to promote strength gain reasonably quickly. A combination of set accelerators with water reducers showed promise of promoting significant strength gain at nearly -10°C (14°F), but at the sacrifice of workability. More work needs to be done to develop a combination of off-the-shelf admixtures that will permit concreting at temperatures as low as -10°C (14°F).					
15. SUBJECT TERMS Antifreeze admixtures Freeze-thaw Cold weather concrete Winter construction					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)
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